Cahn-Landau Theory of First-Order, Critical and Tricritical Wetting at the Liquid-Vapor Interface of n-Alkane/Methanol Mixtures

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A mean-field theory is presented which describes the basic observations of recent experiments [1] revealing rich wetting behaviour of n-alkane/methanol mixtures at the liquid-vapor interface. The theory is based on a microscopic lattice-gas model from which a Cahn-Landau approach is distilled. Besides the physics associated with the short-range components of the intermolecular interactions, effects of the long-range tails of the net van der Waals forces between interfaces are also taken into account.

Further, gravitational thinning of the wetting phase is incorporated. For three different systems the adsorption is calculated as a function of temperature and compared with the experimentally measured ellipticity. Including weak long-range forces which favor wetting in the theory does not visibly alter the critical wetting transition for the nonane/methanol mixture, in contrast with the generic expectation of first-order wetting for such systems, but in good agreement with experiment. For decane/methanol weak long-range forces bring the transition very close to the prewetting critical point, leading to an adsorption behavior closely reminiscent of short-range tricritical wetting, observed experimentally for alkane chain length between 9.6 and 10.

Finally, for undecane/methanol the transition is clearly of first order. First-order wetting is also seen in the experiment.

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1. D. Ross {\em et al}, Phys. Rev. Lett. {\bf 87}, 176103 (2001).